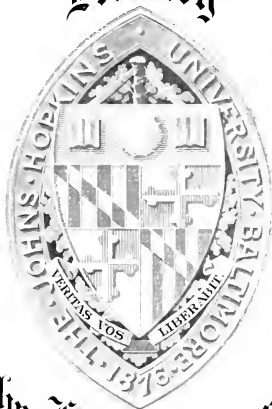


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A FURTHER STUDY  
of two of the  
PRODUCTS OF THE TRANSFORMATION  
of  
PARASULPHAMINEBENZOIC ACID  
when heated to 220°

-:-

Dissertation

submitted to the Board of University Studies of  
the Johns Hopkins University for the degree

of

Doctor of Philosophy

by

Joseph Scudder Chamberlain

1899.



#### ACKNOWLEDGMENT.

The author is glad of an opportunity to express his thanks to Professor Ira Remsen, under whose direction this investigation has been pursued, for his interest and instruction in the work, and also, for his inspiration as a student and his example as a teacher.

Thanks are also due to the other instructors in the University who have assisted the author in his courses, especially to Professors Morse and Renouf, and Doctors Andrews and Matthews.



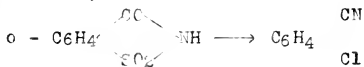
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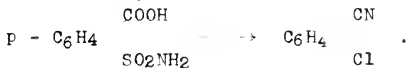


## INTRODUCTION.

The study of the reactions, in which there occurs a shifting of the nitrogen atom in parasulphaminebenzoic acid, has been carried on in this laboratory since 1889, when Remsen and Dohme<sup>1</sup> showed that by the action of phosphorus pentachloride on benzoic sulphinid, orthochlorbenzoic nitrile was formed;



and that parasulphaminebenzoic acid underwent an analogous transformation;



Remsen and Hartman<sup>2</sup> studied the latter reaction more thoroughly and showed that the intermediate product was paracyanbenzenesulphone chloride which, by loss of sulphur dioxide, formed parachlorbenzoic nitrile. They thought that the first step in the transformations, was probably a rearrangement, due to the action of heat upon the parasulphaminebenzoic acid, by which an acid, isomeric with it was formed, and that this acid was acted upon by the phosphorus pentachloride and converted into the parachlorbenzoic nitrile.

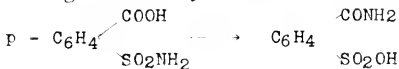
<sup>1</sup>Amer. Chem. Journ. 11, 347.

<sup>2</sup>Hartman, Dissertation, Johns Hopkins University, 1894.  
Amer. Chem. Journ. 18, 150.

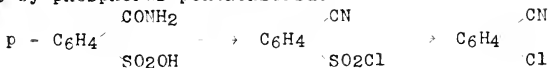




The changes were represented as follows:



and this by phosphorus pentachloride



They attempted to secure the isomeric acid by simply heating parasulphaminebenzoic acid and found that when heated to 235° the parasulphaminebenzoic acid fuses slowly and is converted into soluble acid substances, and that if heated to 285° the chief product is acid ammonium parasulphobenzoate.

The work was here taken up by Remsen and Muckenfuss<sup>1</sup> who showed that when parasulphaminebenzoic acid is heated at 220° for eight hours, there are four products formed:

- (1) Free parasulphobenzoic acid,
- (2) Acid ammonium parasulphobenzoate,
- (3) An infusible substance, isomeric with the ordinary diamide of parasulphobenzoic acid, which they called the infusible diamide and to which was given the formula  $p - \text{C}_6\text{H}_4 \begin{array}{l} \text{CONH}_2 \\ \text{SO}_2\text{NH}_2 \end{array}$ ,
- (4) An acid thought to be isomeric with parasulphaminebenzoic acid, which they called iso-parasulphaminebenzoic acid.

<sup>1</sup>Muckenfuss, Dissertation Johns Hopkins University, 1895.  
Amer. Chem. Journ. 18, 349.



Two years later Stoddard<sup>1</sup> repeated the work of Muckenfuss in order to secure stronger evidence for the formation and supposed constitution of the infusible diamide and the iso-parasulphaminebenzoic acid.

From the results of his work he concluded that the acid which Muckenfuss had called iso-parasulphaminebenzoic acid is not isomeric with ordinary parasulphaminebenzoic acid but is the anhydride, and corresponds to the anhydride of ortho-sulphaminebenzoic acid or benzoic sulphinid,  $C_6H_4 \begin{matrix} \text{CO} \\ \text{SO}_2 \end{matrix} \text{NH}$ .

He also showed that when the infusible diamide is boiled with magnesium hydroxide, there is formed a salt of an acid that is isomeric with parasulphaminebenzoic acid and which may be paracarbaminebenzenesulphonic acid  $p - C_6H_4 \begin{matrix} \text{CONH}_2 \\ \text{SO}_2\text{OH} \end{matrix}$ .

It was in the hope of securing conclusive evidence in regard to these two points, that the following work, largely repeating that of Stoddard, was undertaken.

#### PREPARATION OF MATERIAL.

In the preparation of the material great care was taken in order to secure it pure. Stoddard<sup>2</sup> made the pure parasulphaminebenzoic acid synthetically, by the method used by

<sup>1</sup>Dissertation, Johns Hopkins University, 1897.

<sup>2</sup>Dissertation, p. 6.



Remsen<sup>1</sup>, from paratoluenesulphonamide. He had at first tried to obtain pure acid by direct recrystallization of the commercial product obtained from saccharin. In this investigation all of the parasulphaminebenzoic acid used was obtained from commercial saccharin. It was found, however, that direct recrystallization was not sufficient and the following method of purification through the barium salt was adopted.

The impure residue, left after commercial saccharin has been hydrolyzed by boiling with hydrochloric acid, consists, almost entirely, of parasulphaminebenzoic acid.

This residue was boiled with barium carbonate and converted into the readily soluble barium parasulphaminebenzoate. The barium salt that crystallized from the filtrate was recrystallized from pure water, three times. The purified salt, thus obtained, was dissolved in hot water and hydrochloric acid added, when the difficultly soluble parasulphaminebenzoic acid was thrown down. The acid was filtered off, washed free of barium chloride and hydrochloric acid, and recrystallized from hot water seven times.

The parasulphaminebenzoic acid thus obtained was in the form of beautiful white needles and possessed the properties originally described by Remsen<sup>2</sup>. The melting-point of the

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<sup>1</sup>Ann. Chem. (Liebig) 178, 297.

<sup>2</sup>Ann. Chem. (Liebig) 178, 299.



last five crystallizations was practically identical and was sharp. The melting-point determinations are:

1st recrystallization	288° - 290° (uncorrected)
2nd "	289° - 290°
3rd "	290°
4th "	290°
5th "	289°
6th "	290°
7th "	290°

The melting-point varies considerably according to the rapidity of heating. When heated slowly the acid will melt as low as 280°, while the same sample, if heated rapidly, to within a few degrees of its melting-point, does not melt until it reaches 289° or 290°.

In all of the above determinations however the heating was done, as nearly as was possible, in exactly the same way. To accomplish this, two melting point tubes were placed on either side of the thermometer bulb, one containing acid of one crystallization and the other of another. By determining the melting-points under these conditions accurate comparisons were made. It seems probable that the parasulphaminebenzoic acid finally obtained and worked with was pure. A sample of the acid prepared by Stoddard and also some prepared in this laboratory from parasulphobenzoic acid





through the dichloride and diamide, were compared in the above manner with that used in this investigation, and found to melt at temperatures ranging from  $286^{\circ}$  -  $289^{\circ}$ .

It may be stated here, however, from the results of this investigation, that, so far as concerns the purity and properties of the iso-parasulphaminebenzoic acid and the infusible diamide, it seems to make no difference whether the original parasulphaminebenzoic acid, that is to be heated, is of this exceptional degree of purity or not.

The acid used in the latter part of this investigation was in the state of comparative purity as it is produced by the manufacturers by the hydrolysis of commercial saccharine.

#### HEATING OF PARASULPHAMINEBENZOIC ACID.

It was noticed, early in the work, that when the heating of the parasulphaminebenzoic acid was carried on in an open dish, there was much charring of the product and consequently much purification of the extract was necessary. The heating was therefore done in large test-tubes that were sealed. As the mass of substance was of quite small diameter, it was more readily heated to a uniform temperature and there was less liability of overheating the outer portion. This rather than the sealing of the tubes is the reason why little charring took place.

The most uniform results, too, were secured when the



tubes were heated in a bath of sulphuric acid; but, as this method was objectionable, most of the heating was accomplished by putting the tubes in an ordinary air bath.

#### THE SUBLIMATE.

As noticed by Muckenfuss<sup>1</sup> and Stoddard<sup>2</sup> there is always formed, during the fusion, a crystalline sublimate that collects on the watch glass cover or on the upper parts of the tube. This sublimate was collected from all the fusions made and enough material obtained to study qualitatively. It is very finely crystalline in the form of needles and is slightly soluble in cold water. When dissolved in hot water and allowed to crystallize out the crystals have all the appearance and properties of parasulphaminebenzoic acid. No other substance such as described by Muckenfuss was found. It seems therefore that the crystalline sublimate consists of unchanged parasulphaminebenzoic acid that has been sublimed during the slow heating.

#### EXTRACTION OF FUSED PRODUCT WITH ALCOHOL.

Under the most favorable conditions the fused product, obtained by heating the parasulphaminebenzoic acid for eight hours at 220°, is of a light brown color and consists of the

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<sup>1</sup>Dissertation, p. 25.

<sup>2</sup>Dissertation, p. 7.



four substances isolated by Muckenfuss<sup>1</sup> but the composition and constitution of which are in question.

When this fused product is powdered and extracted with boiling alcohol, there is deposited from the filtrate, on cooling, a flocculent crystalline mass of fine needle-like crystals as noticed by Muckenfuss<sup>2</sup> and Stoddard<sup>3</sup>. These crystals are entirely distinct from the thick prismatic crystals of acid ammonium parasulphobenzoate, that is extracted from the fusion product at the same time, but that is more soluble in alcohol, and remains in solution until the extract is evaporated to a quite concentrated condition. The fine needle crystals first obtained are of neutral reaction and yield ammonia readily in the cold when treated with sodium hydroxide. By adding barium chloride to a solution of the crystals the well characterized barium salt is obtained.

It does not seem clear whether the previous investigators regarded this crystalline substance, obtained from the alcoholic extract of the fusion product, as the free isoparasulphaminebenzoic acid, or not. Muckenfuss<sup>4</sup>, in the

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<sup>1</sup>Dissertation, p. 44.

<sup>2</sup>Dissertation, p. 27.

<sup>3</sup>Dissertation, p. 14.

<sup>4</sup>Dissertation, p. 34.



equations given to represent the reactions supposed to take place, gives to this product the formula of the free acid;  $C_6H_4 \begin{smallmatrix} \text{CONH}_2 \\ \text{SO}_2\text{OH} \end{smallmatrix}$ , while in another place<sup>1</sup> he speaks of the flocculent precipitate as the ammonium salt of the iso-para-sulphaminebenzoic acid. Stoddard<sup>2</sup> speaks of it as the free acid, yet, from his description of the free acid that he prepared from the barium salt by means of sulphuric acid, it seems improbable that he regarded the two substances as the same.

#### THE AMMONIUM SALT OF PARABENZOIC SULPHINIC (?).

The fine needle crystals, obtained as the first crystallization product from the alcoholic extract, were purified by recrystallizing three times from hot alcohol. It was found that while ordinarily, as thrown down from a somewhat concentrated alcoholic solution, the crystals were distinctly needle-shaped, yet, when filtered off and redissolved in alcohol or water and allowed to crystallize slowly from a dilute solution, they were in the form of minute glistening plates that gave to the mass in the liquid a characteristic micaceous appearance. The crystals probably always form as plates but when from a concentrated solution, the plates are very small and arrange themselves in rows and thus give the

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<sup>1</sup>Dissertation, pp. 27, 28.

<sup>2</sup>Dissertation, pp. 14, 15.





appearance of needles.

The salt is very soluble in water but less so in alcohol. It probably contains no water of crystallization as a loss equal to only one half molecule of water was obtained on drying. It yields one half of its nitrogen as ammonia by boiling with magnesium hydroxide and does not yield any more with sodium hydroxide.

Analysis of the Ammonium Salt.

The analyses of the ammonium salt that had been recrystallized are:

0.4194 gms. salt gave at 300°	0.0196 gms. H <sub>2</sub> O
0.0506 " " "	0.0629 gms. BaSO <sub>4</sub> (Carius)
0.0944 " " "	0.1190 " " "
0.0920 " " "	0.1148 " " "
0.0955 " " "	0.01327 " N. (Dumas)
0.1368 " " "	0.01779 " " "
0.2069 " " "	0.0143 " " (by NaOH)
0.1166 " " "	0.00858 " " "
0.1846 " " "	0.01173 " " "



Calculated for C <sub>6</sub> H <sub>4</sub> CO N.NH <sub>4</sub> SO <sub>2</sub>		Calculated for C <sub>6</sub> H <sub>4</sub> CONH <sub>2</sub> SO <sub>2</sub> ONH <sub>4</sub>		Found.
1/2 H <sub>2</sub> O	4.3	4.0		4.72
S	16.0	14.68	17.06, 17.31, 17.13	
N. (total)	14.0	12.84	13.90, 13.00	
N. (one half)	7.0	6.42	6.91, 7.36, 6.35	

The results of these analyses indicate that the salt cannot be purified by recrystallization. The difficulty comes probably from the fact that there is present with the ammonium salt some of the acid ammonium parasulphobenzoate, that is extracted by the alcohol at the same time and that is not removed by recrystallization. An attempt was made to purify the salt by dissolving in water and then adding acetone, but the method did not work well.

#### PREPARATION OF THE AMMONIUM SALT FROM THE BARIUM SALT.

The preceding analyses, while not as good as could be desired, show that the original crystals, obtained from the alcoholic extract of the fused product, are the ammonium salt and not the free acid. It was then desirable to see if an ammonium salt prepared from the barium salt would be the same as the one just studied. In order to test this point the barium salt, prepared as hereafter described<sup>1</sup> and the purity

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<sup>1</sup>This Dissertation, p. 13.



of which had been tested by analysis, was dissolved in water and ammonium sulphate added in slightly less quantity than was required to precipitate all of the barium. The barium sulphate was then filtered off, and the filtrate evaporated. The residue was extracted with alcohol and the crystals separating out were recrystallized. The substance thus obtained resembled in all respects the salt originally obtained from the alcoholic extract of the fused product. In the last analyses the ammonium salt was prepared by using an excess of ammonium carbonate to precipitate the barium, and then driving off the excess of ammonium carbonate from the filtrate by boiling.

Analysis of Ammonium Salt made from  
Barium Salt.

0.0172 gms. salt gave at 300°	0.0078 gms. H <sub>2</sub> O
0.0491 " " "	0.00347 " N. (by NaOH)
0.0983 " " "	0.0158 " " (Dumas)
0.0108 " " "	0.0130 " BaSO <sub>4</sub> (Carius)
0.0655 " " "	0.0763 " " "

Calculated for		Calculated for	Found.
$\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \quad > \text{N} \cdot \text{NH}_4 \\ \diagdown \quad \diagup \\ \text{SO}_2 \end{array}$		$\begin{array}{c} \text{CONH}_2 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \quad > \text{N} \cdot \text{NH}_4 \\ \diagdown \quad \diagup \\ \text{SO}_2\text{ONH}_4 \end{array}$	
1/2 H <sub>2</sub> O	4.3	4.0	4.53
S	16.0	14.68	16.52, 15.99
N (total)	14.0	12.84	16.07
N. (one half)	7.0	6.42	7.06



## PREPARATION OF THE BARIUM SALT.

The crystals of the ammonium salt as they are thrown down from the alcoholic extract of the fusion product, were dissolved in water and barium chloride added. The characteristic barium salt was precipitated in fine needles forming a thick gelatine-like mass. The purification of this salt was accomplished by recrystallizing from hot water. It was difficult to secure samples that seemed pure as indicated by analysis. The reason for this is probably the same as that stated before in the purification of the ammonium salt, that is, the presence in the original extract of the acid ammonium parasulphobenzoate. Several other methods of purification were tried but none worked as well as simple recrystallization. The number of recrystallizations made were as high as nine until the final products gave fairly concordant results.

Analysis of the Barium Salt.

The character of the salt is such that proper drying for determination of the water of crystallization was exceedingly difficult. The crystals are so fine that it is impossible to dry them at once by means of absorbent paper, and the salt loses water so readily that quick drying is absolutely necessary for correct determinations. For this reason, the determinations of water of crystallization vary a great deal and little reliability can be placed upon them. The first





three determinations were made with salt that was dried first on a porous plate until dry enough not to stick to absorbent paper and then pressed between folds of paper until reduced to a fine powder. In the third determination the pressing between papers was not so long as in the other cases. In the fourth, the salt was allowed to remain for a long time on a porous plate in the air. The results obtained are:

I.	0.0984	gms.	salt	lost	at	220°	0.009	gms.	H <sub>2</sub> O
II.	0.050	"	"	"	"	"	0.0048	"	"
III.	0.0691	"	"	"	"	"	0.0075	"	"
IV.	3.2630	"	"	"	"	"	0.1645	"	"

Calculated for			Found.			
(C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> N <sub>2</sub> ) <sub>2</sub> Ba + 3H <sub>2</sub> O	SO <sub>2</sub>		I.	II.	III.	IV.
			9.73	9.14,	9.60,	10.85, 5.04



## BARIUM DETERMINATIONS.

In these determinations the anhydrous salt was used.

Sample. 1st. Series.

I.	0.1655	gms.	salt	gave	0.0768	gms.	BaSO <sub>4</sub>
II.	0.2253	"	"	"	0.1044	"	"
II.	0.2379	"	"	"	0.1097	"	"
II.	0.1551	"	"	"	0.0718	"	"
II.	0.1278	"	"	"	0.0592	"	"
III.	0.1577	"	"	"	0.0725	"	"

2nd. Series.

Recrystal-  
lization.

2	0.1068	"	"	"	0.0473	"	"
3	0.1282	"	"	"	0.0583	"	"
4	0.1680	"	"	"	0.0771	"	"
5	0.0884	"	"	"	0.0400	"	"
6	0.0560	"	"	"	0.0257	"	"
7	0.0758	"	"	"	0.0350	"	"
8	0.1917	"	"	"	0.0887	"	"
9	0.1074	"	"	"	0.0500	"	"
9	0.1159	"	"	"	0.0538	"	"

3rd. Series.

5	0.0669	gms.	salt	gave	0.0298	gms.	BaSO <sub>4</sub>
5	0.0585	"	"	"	0.0260	"	"
6	0.0535	"	"	"	0.0241	"	"
8	0.1261	"	"	"	0.0576	"	"
9	0.0942	"	"	"	0.0431	"	"
9	0.0628	"	"	"	0.0288	"	"
9	(by al- 0.1618	gms.	salt	gave	0.0740	"	"
	cohol)						
9	"	0.1081	"	"	0.495	"	"

Nitrogen Determinations.

0.2142	gms.	salt	gave	0.0121	gms.	N.	(Dumas)
0.1369	"	"	"	0.0082	"	"	"
0.2952	"	"	"	0.01679	"	"	"

Sulphur Determinations.

0.1301	gms.	salt	gave	0.1123	gms.	Ba SO <sub>4</sub>	(Carius)
0.1455	"	"	"	0.1382	"	"	"
0.1311	"	"	"	0.1230	"	"	"
0.0898	"	"	"	0.0867	"	"	"



## RESULTS OF ANALYSIS.

Calculated for	Ba.	S.	N.
$\begin{array}{c} \text{CO} \\ \swarrow \quad \searrow \\ (\text{C}_6\text{H}_4) \quad \text{N})_2 \text{ Ba} \\ \quad \quad \quad \searrow \\ \quad \quad \quad \text{SO}_2 \end{array}$	27.34	12.77	5.59

Calculated for	Ba.	S.	N.
$\begin{array}{c} \text{CONH}_2 \\ \swarrow \quad \searrow \\ (\text{C}_6\text{H}_4) \quad \text{SO}_2\text{O} \end{array}$	25.51	11.91	5.21

## Found.

## Sample.

1st. Series	I.	27.25		
	II.	27.24	12.59	5.63
	II.	27.11	13.03	
	II.	27.22	12.88	5.98
	II.	27.24		5.68
	III.	27.03	13.25	

## Recrystallization.

2nd. Series	2	26.04
	3	26.74
	4	26.98
	5	26.60
	6	27.00
	7	27.15
	8	27.20
	9	27.37
	9	27.29
3rd. Series.	5	26.19
	5	26.15
	6	26.48
	8	26.85
	9	26.90
	9	26.96
	9 (by alcchol)	26.89
	9	26.92



## THE COPPER SALT.

The only salts heretofore studied have been the barium and sodium salts.

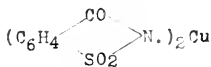
By adding copper sulphate, to a solution of the barium salt, in slightly less quantity than required to precipitate all of the barium, and filtering off the barium sulphate, the filtrate, ~~on evaporation~~ nearly to dryness, yields small bunches of blue crystals. On removing the crystals from the viscous mother-liquor they become pasty and on drying cake up into hard masses. The salt was dried at  $150^{\circ}$  and analyzed for copper.

0.1022 gms. salt gave

0.0191 gms CuO.

Calculated for

Found



Cu.

14.75

14.80

## THE LEAD SALT.

The lead salt was made from the free sulphinid,<sup>1</sup> prepared by precipitating all of the barium, from a solution of the barium salt, by means of sulphuric acid. A solution of the free sulphinid, thus obtained, was boiled with lead carbonate and the excess of carbonate filtered off. On evaporating the filtrate crystals separated but were too indistinct to make out their form. They did not become pasty

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<sup>1</sup>This Dissertation, p. 18.





and cake up in hard masses as the copper salt. The salt was analyzed for water and for lead.

0.0768 gms. salt gave at 170°	0.0067 gms. H <sub>2</sub> O
0.0697 " " "	0.0333 " PbSO <sub>4</sub>
0.0791 " " "	0.0377 " "

Calculated for

$\begin{array}{c} \text{CO} \\ \diagup \\ (\text{C}_6\text{H}_4 \text{---} \text{N.})_2 \text{ Pb} \\ \diagdown \\ \text{SO}_2 \end{array}$	
+3H <sub>2</sub> O	8.72
Pb	36.24      35.74,    34.37

#### FREE PARABENZOIC SULPHINID.

Attempts were made to obtain the free sulphinid in a well crystallized form, but in every case results were obtained similar to that of Stoddard<sup>1</sup> and no sample was obtained that could be submitted to analysis.

An attempt was also made to study the action of phosphorus pentachloride upon the free sulphinid, to see if results might be obtained analogous to those of Remsen and Dohme<sup>2</sup> with ortho-benzoic sulphinid. The sulphinid was heated with phosphorus pentachloride in a small bulb to 95° but no apparent action took place and no parachlorbenzoic nitrile distilled over. Further heating was tried at higher temperatures but no definite products were obtained. The

<sup>1</sup>Dissertation, p. 15

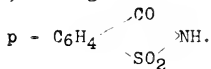
<sup>2</sup>Amer. Chem. Jour. 11,347.



amount of substance used however was very small.

#### DISCUSSION OF PARABENZOIC SULPHINID.

From the results of the analyses, especially those of the barium and ammonium salts, when we consider the character of the salts, that renders their preparation in a pure form for analysis, very difficult, it seems very probable, to say the least, that they are derived from parabenzoic sulphinid, analogous to orthobenzoic sulphinid.



#### PREPARATION OF DIAMIDE.

After the fusion-product, obtained by heating parasulphaminebenzoic acid to  $220^\circ$ , had been extracted with alcohol and all of the ammonium parabenzoic sulphinid removed, the residue was shaken thoroughly with a small quantity of cold water. This removed all traces of ammonium parabenzoic sulphinid and also acid ammonium parasulphobenzoate. The residue, after filtration, was dissolved in cold dilute sodium hydroxide and decolorized by means of animal charcoal. After filtering off the charcoal the diamide was precipitated from the clear liquid by addition of hydrochloric acid. The diamide thus obtained was pure white and when thrown down slowly, from a somewhat dilute solution, the crystals were in the form of thin, almost square, plates. If, how-



ever, crystallization took place suddenly, from a concentrated solution, the plates evidently arranged themselves in rows and appeared as needles. This same peculiarity of crystallization was noticed in the case of the ammonium parabenzonic sulphinid.<sup>1</sup> The identity of the two crystal forms of the diamide was proven beyond a doubt by repeated transformations ~~back and forth from~~ one form to the other.

The pure diamide obtained agrees in all respects with that described by Muckenfuss<sup>2</sup> and Stoddard<sup>3</sup>. It is infusible, very slightly soluble in cold water, more soluble in hot, and insoluble in acids or alcohol and other organic solvents. It is readily soluble in sodium hydroxide and barium hydroxide,<sup>4</sup> yielding ammonia even in the cold. With magnesium hydroxide and potassium carbonate<sup>5</sup> it yields one half of its nitrogen, as ammonia, on boiling.

#### ANALYSIS OF DIAMIDE.

In the following analyses of the diamide, nitrogen was determined by distilling from sodium hydroxide and collecting the ammonia liberated in standard acid solution. The excess of acid was then determined by titration with standard alkali.

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<sup>1</sup>This dissertation, p. 9.

<sup>2</sup>Dissertation, p. 12.

<sup>3</sup>Dissertation, p. 7.

<sup>4</sup>This dissertation, p. 28.

<sup>5</sup>This dissertation, p. 25.



0.2631 gms diamide gave 0.03557 gms N.

0.3851 " " " 0.05502 " "

0.2912 " " " 0.04171 " "

0.3298 " " " 0.04686 " "

0.1705 " " " 0.02467 " "

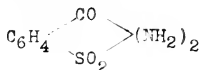
Also by Dumas' method

0.2641 gms diamide gave 0.03655 gms N.

0.3101 " " " 0.04324 " "

Calculated for

Found



N.	14.00	13.48, 14.28, 14.32, 14.21, 14.46
		(Dumas) 13.84, 13.94

Stoddard<sup>1</sup> found that when the infusible diamide is boiled with magnesium hydroxide, there is only one half of the total nitrogen liberated as ammonia. Determinations of nitrogen, by this method gave the following results:

0.4170 gms diamide gave	0.03017 gms N.
0.6553 " " "	0.04810 " "
0.6580 " " "	0.04845 " "
0.4795 " " "	0.03496 " "
1.8825 " " "	0.13525 " "
1.7765 " " "	0.12709 " "
3.4585 " " "	0.2365 " "

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<sup>1</sup>Dissertation, p. 9.





Calculated for		Found
	CO.	
	C <sub>6</sub> H <sub>4</sub> (NH <sub>2</sub> ) <sub>2</sub>	
	SO <sub>2</sub>	
1/2N.	7.0	7.23, 7.34, 7.36, 7.29
		7.18, 7.15, 6.84

These results agree with those of Muckenfuss<sup>1</sup> and leave no room for doubt that the infusible diamide is isomeric with <sup>the</sup> ordinary diamide and further, as shown by the action of magnesium hydroxide and later by the action of potassium carbonate<sup>2</sup> it contains two nitrogen atoms that are evidently not in the same condition.

#### THE MAGNESIUM SALT.

When the infusible diamide is boiled with magnesium hydroxide there is, at first, a rapid evolution of ammonia and, as shown by the analyses, the ammonia liberated is equivalent to only one half of the nitrogen contained in the diamide. With long continued boiling only a very slight excess over the calculated amount of nitrogen could be obtained and these slight excesses were probably due to impurities or to the long continued boiling in glass vessels. It is quite certain that none of the second atom of nitrogen is removed by magnesium hydroxide.

After the ammonia had all been driven off from the solution containing diamide and magnesium hydroxide, the excess

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<sup>1</sup>Dissertation, p. 9.

<sup>2</sup>This dissertation, p. 25.



of magnesium hydroxide was removed by filtration and the filtrate evaporated. From the concentrated solution crystals of the magnesium salt separated that agreed in all respects with those of Stoddard.<sup>1</sup>

The salt crystallizes in small diamond-shaped crystals that are readily soluble in water but insoluble in alcohol or ether. It yields ammonia by warming with sodium hydroxide but not with potassium carbonate<sup>2</sup>. After all nitrogen has been liberated by sodium hydroxide, neutral sodium parasulphobenzoate was formed as was recognized by transformation into the characteristic acid barium salt.

#### . ANALYSIS OF MAGNESIUM SALT.

It was found that magnesium could not be determined by direct ignition to the oxide and it was therefore determined by dissolving the salt in water and precipitating the magnesium as magnesium ammonium phosphate and subsequent ignition to pyrophosphate. The results of the analyses are:

0.3748	gms	salt	gave	0.0535	gms	H <sub>2</sub> O
0.1757	"	"	"	0.0459	"	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
0.2230	"	"	"	0.0570	"	"
0.2201	"	"	"	0.01492	"	N. (Dumas)
0.0982	"	"	"	0.1089	"	BaSO <sub>4</sub> (Carius)

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<sup>1</sup>Dissertation, p. 11.

<sup>2</sup>This dissertation, p. 26.



Calculated for		Found	
$\begin{array}{c} \text{CO.} \\ (\text{C}_6\text{H}_4 \text{---} \text{NqH}_2) \text{SO}_2 \end{array} \text{)}_2 \text{ Mg}$			
4 H <sub>2</sub> O	14.52	14.27	
Mg.	5.66	5.64,	5.52
N.	6.60	6.78	
S.	15.09	15.22	

### THE POTASSIUM SALT.

By treating a solution of the magnesium salt with potassium carbonate and filtering off the precipitated magnesium carbonate, ~~there is obtained, on evaporation of the filtrate,~~ crystals of the potassium salt, as described by Stoddard,<sup>1</sup>

In the formation of this salt and evaporation of the filtrate there is no evolution of ammonia.

The potassium salt is very characteristic, forming beautiful, clear, spindle-shaped crystals that remain wholly separate from each other unless the solution is too concentrated. They contain no water of crystallization and are readily soluble in water. By warming with sodium hydroxide ammonia is given off just as in the case of the magnesium salt.

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<sup>1</sup>Dissertation p. 12.

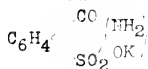


## ANALYSIS OF THE POTASSIUM SALT.

0.1192	gms.	salt	gave	0.0426	gms	$K_2SO_4$
0.2526	"	"	"	0.0911	"	"
0.0609	"	"	"	0.0207	"	"
0.0505	"	"	"	0.0180	"	"
0.2711	"	"	"	0.01654	"	N (Dumas)
0.0962	"	"	"	0.0962	"	$BaSO_4$ (Carius)

Calculated for

Found



K.	16.32	16.06, 16.20, 16.01, 16.02
N.	5.86	6.10
S.	13.39	13.73

## ACTION OF POTASSIUM CARBONATE ON DIAMIDE.

Stoddard<sup>1</sup> states that sodium carbonate liberates more than one half of the nitrogen from the diamide, on boiling. This appeared strange, from the fact that if one half of the nitrogen is first liberated from the diamide by boiling with magnesium hydroxide, a magnesium salt is formed, containing the remaining atom of nitrogen, and this atom of nitrogen is not driven out from the magnesium salt by means of potassium carbonate. If then the nitrogen is all driven out of the diamide by potassium carbonate and not at all from the mag-

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<sup>1</sup>Dissertation, p. 9.





nesium salt, the one atom of nitrogen in the magnesium salt is evidently in a different condition from that which it occupied in the diamide. It seemed therefore that by boiling the diamide with potassium carbonate we ought to be able to obtain the same salt that is formed indirectly from the diamide through the magnesium salt. In order to test this point the following experiments were made:

I. One portion of diamide was treated with the calculated quantity of potassium carbonate, sufficient to replace one atom of nitrogen and another portion was treated with double this quantity. Both solutions on boiling gave off ammonia and on evaporation deposited crystals. In both cases, however, the crystals that separated were identical and exactly corresponded to those obtained from the magnesium salt. In neither case was any trace of neutral potassium sulphobenzoate observed nor of any other salt than the one mentioned.

II. Two portions of the magnesium salt<sup>1</sup> prepared from the diamide by magnesium hydroxide, were taken. One portion was treated with the calculated amount of potassium carbonate sufficient to replace the magnesium and the other with double this amount. In neither case was there any evidence of liberation of ammonia and from both solutions the same potassium salt crystallized which was identical

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<sup>1</sup>This dissertation, p. 22.



with that obtained in the first experiment. The identity of all of these salts was corroborated by analysis.

It is thus shown that potassium carbonate does not liberate more than half of the nitrogen of the diamide, and that the nitrogen atom in the magnesium and potassium salts is undoubtedly in the same condition ~~that it is~~ in the diamide. The potassium salt therefore is obtained much more easily by boiling the diamide directly with potassium carbonate.

#### THE BARIUM SALT.

It was found that, when the potassium salt, in solution, was treated with the calculated amount of barium chloride, sufficient to replace the potassium, on evaporation of the solution a little, crystals separated out that had every appearance of the potassium salt but that were found to contain barium. They are clear, and spindle-shaped, but are less soluble than the potassium salt and are thrown down from a more dilute solution not separate but grouped together in clusters.

The salt contains no water of crystallization and gives off ammonia when heated with sodium hydroxide, but not with potassium carbonate. The solution is not precipitated by addition of hydrochloric acid. After ammonia has been driven off by sodium hydroxide, hydrochloric acid precipi-



tates the characteristic acid barium parasulphobenzoate.

#### ANALYSIS OF THE BARIUM SALT.

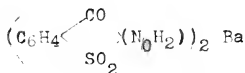
0.0397 gms salt gave 0.0173 gms  $\text{BaSO}_4$

0.0728 " " " 0.0641 "  $\text{BaSO}_4$  (Carius)

0.0991 " " " 0.00583 " N. (Dumas)

Calculated for

Found.



Ba.	25.51	25.62
S.	11.91	12.09
N.	5.21	5.80

#### ACTION OF BARIUM HYDROXIDE UPON <sup>THE</sup> DIAMIDE.

It was found that barium hydroxide readily dissolved the diamide and that, after standing a while, the solution gave off ammonia, even in the cold. It was thought, therefore, that the barium salt could probably be prepared in this way. A portion of diamide was placed in a flask, ~~and~~ and an excess of barium hydroxide solution added, and the whole solution kept cool by surrounding the flask with water. In order to carry off the ammonia that was liberated, a current of air, free of carbon dioxide and ammonia, was drawn through the solution and into a solution of standard sulphuric acid. In this way some indication could be obtained of the amount of ammonia given off. The action was allowed



to continue until approximately the equivalent of one half of the nitrogen had been set free from the diamide.

The excess of barium hydroxide was then removed from the solution by carbon dioxide and the filtrate evaporated to crystallization. During the evaporation some unchanged diamide separated out and also some acid barium parasulphobenzoate.

When the solution had been evaporated nearly to dryness quite a quantity of crystalline substance separated, but this proved to be almost pure neutral barium parasulphobenzoate. No evidence of any other crystalline product was found. A striking feature of the experiment, however, was that the concentrated mother-liquor, after the neutral barium parasulphobenzoate had crystallized out, seemed to contain a substance rich in nitrogen. On treating the mother-liquor with sodium hydroxide there was an abundant evolution of ammonia at once. The ammonia was given off much more easily than from the diamide and the quantity seemed much greater than would have been obtained from the quantity of diamide that could have been held in solution in the amount of liquid present.

All efforts to isolate a new salt from the solution failed.

Barium hydroxide therefore acts as sodium hydroxide

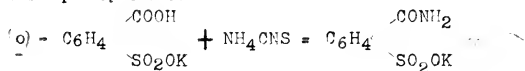




and liberates all of the nitrogen from the diamide forming the neutral parasulphobenzoate and no intermediate salt, containing one atom of nitrogen, was obtained in this way. It seems possible that the barium hydroxide may have formed a very soluble salt with the diamide without driving out any of the nitrogen.

#### PREPARATION OF POTASSIUM PARACARBAMINEBENZENESULPHONATE (?)

Wilson<sup>1</sup> has been studying in this laboratory the salts of orthocarbaminebenzenesulphonic acid. The method used is one obtained from patent literature:consisting of heating a mixture of acid potassium orthosulphobenzoate and ammonium sulphocyanate.



The same reaction was therefore tried with the para compound, to see if paracarbaminebenzenesulphonic acid salts could be obtained and to compare them with the salts obtained from the diamide.

Acid ammonium parasulphobenzoate was prepared by the hydrolysis, in a sealed tube, of parasulphaminebenzoic acid. The ammonium salt thus obtained was converted into the corresponding potassium salt.

A quantity of the acid potassium parasulphobenzoate was then mixed with about twice the theoretical amount of ammo-  
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1Dissertation, Johns Hopkins University, 1899.

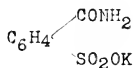


nium sulphocyanate and heated for several days, first just to the fusion point, and later to  $200^{\circ}$ . The product was then powdered and dissolved in water, all but a small amount of sulphurous matter going into solution readily. The solution was decolorized by boiling with animal charcoal and the filtrate evaporated to crystallization. Crystals ~~did not form~~ until the solution was quite concentrated, when fine short needles or prisms separated which are distinctly different from the clear spindle-shaped crystals obtained from the diamide by boiling with potassium carbonate.<sup>1</sup> The crystals come down in masses and are not separate and distinct in form. The salt yields ammonia when heated with sodium hydroxide or barium hydroxide but not with potassium carbonate. It contains no water of crystallization.

#### ANALYSIS OF THE POTASSIUM SALT.

0.0659 gms. salt gave	0.0306 gms. $K_2SO_4$
0.0522 " " "	0.0535 " $BaSO_4$ (Carius)
0.1017 " " "	0.0126 " N. (Dumas)

Calculated for



Found.

K.	16.32	16.01
S.	13.39	14.07
N.	5.86	12.39

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<sup>1</sup>This dissertation, p. 25



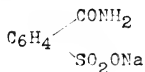
## THE SODIUM SALT.

The sodium salt was prepared in exactly an analogous way. The salt did not crystallize except from a very concentrated solution and the crystals were indistinct as in the case of the potassium salt. One analysis for sodium was made.

0.0597 gms. salt gave 0.0191 gms.  $\text{Na}_2\text{SO}_4$

Calculated for

Found.



Na. 10.31

10.37

## THE SILVER SALT.

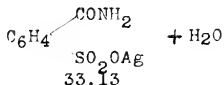
From the sodium salt the silver salt was prepared by adding to a solution of the salt in water the calculated amount of silver nitrate sufficient to replace the sodium.

The silver salt crystallized out in star-like clusters of thin leaves or plates that darken in the light. The crystals were removed dried quickly with paper and analyzed for silver.

0.0139 gms. salt gave 0.0046 gms. Ag.

Calculated for

Found



Ag.

33.13

33.09



## THE BARIUM SALT.

By adding barium chloride to a solution of the potassium salt it was thought that the barium salt might be formed and crystallize out before the potassium salt, as in the case of the corresponding salts obtained from the diamide. The barium salt did not crystallize out in anything that looked like a pure form. The salt was certainly not the same as was obtained from the diamide<sup>1</sup> through the potassium salt. It gave ammonia with sodium hydroxide and with barium hydroxide.

Further evidence in regard to these salts, as to whether or not they are salts of a carbamine acid, was not obtained in this study.

It may be stated that Nakaseko<sup>2</sup> has found that in the meta compound, entirely different reactions take place, when heated with ammonium sulphocyanate, from those found to take place with the ortho compound. The same fact may be true in the case of the para compound.

## DISCUSSION.

From the results of the analyses of the barium and ammonium salts<sup>3</sup> it seems strongly probable that Stoddard<sup>4</sup> was

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<sup>1</sup>This dissertation, p. 27.

<sup>2</sup>Dissertation, Johns Hopkins University, 1899.

<sup>3</sup>This dissertation, pp. 11, 12, 16.

<sup>4</sup>Dissertation, p. 24.





right in giving to the substance, which Muckenfuss<sup>1</sup> had called the isoparasulphaminebenzoic acid, the anhydride or sulphinid formula,  $p - C_6H_4 \begin{matrix} \swarrow CO \\ \searrow SO_2 \end{matrix} NH$ .

It is therefore para benzoic sulphinid and is formed, not as the free sulphinid, but as the ammonium salt, when parasulphaminebenzoic acid is heated to 220°.

That the salts are parabenzoic sulphinid compounds and not carbaminesulphonic acid salts is further strengthened by the fact mentioned by Muckenfuss<sup>2</sup> that the barium salt gives off no ammonia by boiling with sodium hydroxide and also by the fact<sup>3</sup> that the ammonium salt gives one half of its nitrogen as ammonia when heated with magnesium hydroxide but the remaining atom of nitrogen is not removed even by boiling with sodium hydroxide. That the compound is not the isoparasulphaminebenzoic acid, that is, paracarbaminebenzenesulphonic acid, is also indicated by the fact, that two barium salts were obtained, one from the infusible diamide and one by means of the carbamine reaction with ammonium sulphocyanate. These two salts, whether the evidence in regard to their identity is conclusive or not, are certainly distinctly different from the barium salt of parabenzoic sulphinid.

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<sup>1</sup>Dissertation, p. 31.

<sup>2</sup>Ibid, pp. 29, 31.

<sup>3</sup>This dissertation, p. 10.



Whether either or both of these series of salts, obtained in the manner indicated, are true carbaminebenzenesulphonic acid salts, is still a question. That the salts obtained from the infusible diamide still hold in combination one nitrogen atom, that is not in the sulphamine grouping, is certain and it thus seems very probably that it is in the carbamine grouping and that the salts are true isomers of those of parasulphaminebenzoic acid.

In regard to the salts made by heating acid potassium parasulphobenzoate with ammonium sulphocyanate, further investigation is necessary to establish their composition and constitution.

Little evidence has been obtained in regard to the constitution of the infusible diamide. That the two nitrogen atoms are in different conditions appears certain and yet it is improbable that either one is in the sulphamine condition.

A further study and comparison of the salts made from the diamide and those made by the ammonium sulphocyanate reaction may furnish evidence in regard to the condition of one of the nitrogen atoms in the diamide, for the nitrogen atom which remains in the salts is probably in the same condition as it is in the diamide.



## BIOGRAPHICAL SKETCH.

Joseph Scudder Chamberlain was born at Hudson, Ohio, March 7th, 1870.

In 1881 he moved with his parents to Columbus, Ohio, and in 1887 to Ames, Iowa.

He entered the Iowa State College in 1887, and received the degree of B.S. in 1890. He was then appointed Assistant in Chemistry and remained in that position until 1894 when he received the degree of M.S. He returned to the same institution in 1894, as Instructor in Chemistry, remaining until 1897.

He entered Johns Hopkins University as a Graduate Student in 1894, remaining for only a few months each year until 1897.

His subjects were Chemistry, Biology and Geology.

In January, 1898, he was appointed University Scholar, and in June, 1898, University Fellow in Chemistry.









































































